Claims

1. A method for the preparation of a steroid modified solatriose of general formula (I):

Formula (I)

wherein R^1 represents a steroid or a derivative thereof having a hydroxyl group in 3-position and no further unprotected hydroxyl groups; and R^2 represents a straight or branched C_{1-4} alkyl group or a hydroxyl group, which method comprises the step of: reacting a compound of general formula (XIII):

$$OR^4$$
 OR^4
 OR^6
 OR^6
 OR^6
 OR^6
 OR^6
 OR^6
 OR^6
 OR^8
 OR^4
 OR^4
 OR^4
 OR^4
 OR^6
 OR^8
 OR^6
 OR^8
 OR^8
 OR^8

Formula (XIII)

wherein each R⁴ independently represents a benzoyl, acetyl or pivolyl protecting group; R⁶ represents a pivolyl protecting group; R⁸ represents a chloroacetyl protecting group; R⁹ represents a benzoyl, acetyl or pivolyl protecting group; and Tf represents a triflate leaving group;

with a compound of general formula (XIV):

HO-R1

Formula (XIV)

wherein R¹ is as defined above to yield a compound of general formula (XV):

Formula (XV)

wherein R¹, R⁶, R⁸ and R⁹ are as defined above.

2. The method according to claim 2, further comprising the step of: reacting galactose to yield a galactose fully protected with ester type protecting groups, and subsequently treating with hydrogen bromide or hydrogen chloride to yield a compound of general formula (II):

Formula (II)

wherein R³ represents a chlorine or bromine atom; and R⁴ is as defined in claim 1.

3. The method according to claims 1 or 2, further comprising the step: reacting a compound of general formula (II) as defined in claim 2, with a compound of general formula (III):

Formula (III)

wherein R^5 represents a straight or branched C_{1-14} alkyl group or a phenyl group optionally substituted with one or more C_{1-4} alkyl groups whereby the C1-14 alkyl groups are preferably selected from methyl, ethyl and propyl and the phenyl group is preferably selected form phenyl, p-methylphenyl and p-chlorophenyl; and methyl, ethyl and propyl are particularly preferred; to yield a compound of general formula (IV):

Formula (IV)

wherein R⁴ is as defined in claim 1, and R⁵ is as defined above.

4. The method according to any of claims 1 to 3, further comprising the step of: deprotecting a compound of general formula (IV) as defined in claim 3 to yield a compound of general formula (V):

Formula (V)

wherein R⁵ is as defined in claim 3.

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5. The method according to any of claims 1 to 4, further comprising the step of: selectively protecting the OH group in the 6-position of a compound of formula (V) as defined in claim 4 with pivolyl chloride using standard conditions to yield a compound of general formula (VI):

Formula (VI)

wherein R^5 in claim 3; and R^6 is a pivolyl, benzoyl or substituted benzoyl protecting group, whereby the substituents are selected from alkyl groups such as methyl, halogen atoms such as Cl, Br, F, and I and NO_2 .

6. The method according to any of claims 1 to 5, further comprising the step of: selectively protecting the OH groups in 3- and 4-position with a ketal or acetal protecting type protecting group using standard conditions, to yield a compound of general formula (VII):

Formula (VII)

wherein R⁵ and R⁶ are as defined in claims 3 and 5, respectively; and R⁷ represents a ketal or acetal type protecting group selected from the group consisting of benzylidene, 4-nitrobenzylidene, 4-methoxybenzylidene and isopropylidene.

7. The method according to any of claims 1 to 6, further comprising the step of:

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protecting the OH group in 2-position of the compound of general formula (VII) as defined in claim 6 with chloroacetyl chloride using standard conditions, to yield a compound of general formula (VIII):

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Formula (VIII)

wherein R⁵, R⁶ and R⁷ are as defined in claims 3, 5 and 6, respectively; and R⁸ represents a chloroacetyl protecting group.

8. The method according to any of claims 1 to 7, further comprising the step of: selectively deprotecting the OH group in 3- and 4-position of the compound of general formula (VIII) as defined in claim 7 using standard conditions, to yield a compound of general formula (IX):

Formula (IX)

wherein R⁵, R⁶, and R⁸ are as defined in claims 3, 5 and 7, respectively.

9. The method according to any of claims 1 to 8, further comprising the step of: reacting the compound of general formula (IX) with a trialkylorthoacetate, benzoate or pivolate to form an 3,4-orthor ester which is subsequently

migrated to the axial 4-position under acidic conditions to yield a compound of general formula (X):

Formula (X)

wherein R⁵, R⁶, R⁸ and R⁹ are as defined in claims 3, 5, 7 and 1 respectively.

10. The method according to any of claims 1 to 9, further comprising the step of: reacting the OH group in 3-position of the compound of general formula (X) as defined in claim 9 with a protected halogen glucose derivative of general formula (XI):

Formula (XI)

wherein R⁴ is as defined in claim 1; and R¹⁰ represent a halogen atom, a trichloroacetimidiate group, or a thioalkyl group having 1 to 14 carbon atoms, to yield a compound of general formula (XII):

Formula (XII)

wherein R^4 , R^5 , R^6 , R^8 and R^9 are as defined in claims 1, 3, 5, 7 and 9, respectively.

- 11. The method according to any of claims 1 to 10, further comprising the step of: activating the compound of general formula (XII) as defined in claim 10 by oxidizing the thio ether group to a sulfoxide using hydrogen peroxide, and subsequently treating the resulting intermediate with triflic anhydride, to yield a compound of general formula (XIII) as defined in claim 1.
- 12. The method according to any of claims 1 to 13, further comprising the step of: selectively deprotecting the OH group in the 2-position of the compound fo general formula (XV) as defined in claim 1 using thio urea in the presence of a sterically hindered non-nucleophilic base, and subsequently reacting the resulting intermediate with a protected halogen rhanmose derivative of general formula (XVI):

Formula (XVI)

wherein R², R⁴ and R¹⁰ are as defined in claims 1 and 10, respectively; to yield a compound of general formula (XVII):

Formula (XVII)

wherein R¹, R², R⁴, R⁶, and R⁹ are as defined in claims 1, 5 and 9, respectively.

- 13. The method according to any of claims 1 to 12, further comprising the step of: deprotecting the compound of general formula (XVII) as defined in claim 12, to yield the compound of general formula (I) as defined in claim 1.
- 14. The method according to any of the preceding claims, wherein R¹ represents a tomatidin-3-yl, demissidin-3-yl, solanidin-3-yl and solasodin-3-yl group.
- 15. The method according to claims any of the preceding claims, wherein R² represents a methyl group.
- 16. The method according to any of the preceding claims, wherein R³ in the compound of general formula (II) represents a bromine atom.
- 17. The method according to any of the preceding claims, wherein R⁴ in the compound of general formula (II) represents an acetyl protecting group.
- 18. The method according to any of the preceding claims 1, wherein R⁵ in the compound of general formula (III) represents a phenyl group.
- 19. The method according to any of the preceding claims, wherein R⁷ in the compound of general formula (VII) represents a isopropylidene protecting group.
- 20. The method according to any of the preceding claims, wherein R⁴ in the compounds of general formula (XI) and/or compound of general formula (XVI) represents a benzoyl protecting group.

- 21. The method according to any of the preceding claims, wherein reacting a compound of general formula (XIII) with a compound of general formula (XIV) is carried out in the presence of sterically hindered non-nucleophilic base.
- 22. The method according to claim 21, wherein the sterically hindered non-nucleophilic base is selected from 2,6-lutidine, 2,4,6-collidine or 2,6-di-tertbutyl-4-methyl pyridine.
- 23. A steroid modified solatriose of general formula (I) as defined in claims 1 or 15, wherein R¹ represents a tomatidin-3-yl or demissidin-3-yl group.
- 24. A compound of general formula (XVII) as defined in claims 12 or 15.
- 25. A compound of general formula (XV) as defined in claims 1 and 15.
- 26. A compound of general formula (X) as defined in claim 9.
- 27. A compound of general formula (XII) as defined in claim 10.